



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C09K 11/06, G11B 3/70, 7/24	A1	(11) International Publication Number: WO 99/24527 (43) International Publication Date: 20 May 1999 (20.05.99)
(21) International Application Number: PCT/US98/23625 (22) International Filing Date: 6 November 1998 (06.11.98) (30) Priority Data: 60/064,388 7 November 1997 (07.11.97) US (71) Applicant (for all designated States except US): OMD DEVICES LLC [US/US]; Berezowsky, Leonardo, 1013 Centre Road, Wilmington, DE 19805 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): ALPEROVICH, Mark [IL/IL]; Hamelech Hizkija 33/3, 77497 Ashdod (IL). GLUSHKO, Boris [IL/IL]; Melech Rechavam Street 20/8, Rova Gimel, 77480 Ashdod (IL). KRUPKIN, Vladimir [IL/IL]; Ashdod (IL). LEVICH, Eugene [IL/US]; Apartment 9L, 330 West 45 Street, New York, NY 10036 (US). SUL, Irene [IL/IL]; Ashdod (IL). (74) Agents: COHEN, Herbert et al.; Blank Rome Comisky & McCauley LLP, Wigman, Cohen, Leitner & Myers, Intellectual Property Group, 900 17th Street, N.W., Washington, DC 20006 (US).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: FLUORESCENT COMPOSITION FOR THE MANUFACTURE OF CD-ROM TYPE OPTICAL MEMORY DISKS (57) Abstract <p>A CD-ROM type optical disk, whether single-layer or multi-layer, is formed on a substrate having pits in its surface. The pits are filled with a fluorescent composition. Multiple disks such as that one can be glued on top of one another. Suitable fluorescent compositions include xanthene dyes of the eosine group, xanthene dyes of the rhodamine group, acridine dyes, oxazine dyes, azine dyes, indigoide dyes, perylene dyes, violanthrone dyes, cyanine dyes, phthalocyanine dyes, and porphyrins.</p>		

FLUORESCENT COMPOSITION FOR THE MANUFACTURE OF CD-ROM TYPE OPTICAL MEMORY DISKS

FIELD OF THE INVENTION

5 This invention relates generally to optical materials for, and to a method of, forming optical memory discs of the CD-ROM type for use with fluorescent reading, including disks for three-dimensional (3D) optical memory systems.

BACKGROUND OF THE INVENTION

 To date, digital information carriers for recording, storing, and reading sound and
10 images by optical methods have received wide recognition.

 Generally, information is written in the form of local changes to the active medium optical thickness or the reflection coefficient, while reading is performed using laser emission and is based on the laser beam phase or amplitude changes in information record centers.

 CD-ROM's are the least expensive and most sophisticated of the optical information
15 carriers. However, both the storage volume and the signal-to-noise ratio of currently used CD-ROM's are inadequate for the new generations of computers and video systems now under development.

 Therefore, materials for better optical memory systems are being actively developed. These materials are required to provide an increased data density, a high signal-to-noise ratio,
20 an improved operation and storing stability, and low costs.

 A promising approach to the increase of optical information carrier capacity consists of

3D optical memory medium where multilayer data writing and fluorescent reading are performed. With these materials, information is written by the two-photon excitation of the initial non-fluorescing form A of the photochromic compound, this excitation being produced by two focused laser beams intersecting in definite locations of active medium.

5 Under excitation, form A transforms to form B. Form B absorbs two reading emission photons and emits the fluorescent light which is absorbed by a detector. Materials of this type are intended for repeatedly rewritten memory, because heating or irradiation results in erasing data due to the transformation of form B to initial form A.

A practical implementation of 3D optical memory concepts and methods, as suggested
10 by US Patent No. 5,268,862, is quite problematic and highly improbable for a number of reasons, including, in particular, the following:

1. A low photochemical and thermal stability of suggested photochromic compounds resulting in their destruction after repeated writing – reading – erasing cycles.
2. The possibility of erasing data (form B to form A transition) in the process of
15 fluorescence reading.
3. A low quantum yield of merocyanine form B of suggested photochromic spiropyrans.

For the above reasons, the 3D optical memory devices proposed in US Patent 5,268,862 are unsuitable for CD ROM type multilayer disks as well.

20 The use of organic dyes in optic WORM disks is known D.J. Gravesteyn, J. van der Veen, *Philips Tech. Rev.*, **41** (1983/1984), 325; J.E. Kuder, *J. Imag. Technol.*, **12** (1986), 140; J.E. Kuder, *J. Imag. Sci.*, **32** (1988), 51.

Therefore, dye layers, both with and without a polymer binder, used in WORM disks with the reading based on the variation of reflection coefficient, cannot be used in optical CD-ROM type memory disks with a fluorescence reading.

5 SUMMARY OF THE INVENTION

It is an object of the invention to provide a fluorescence-based reading method that has a number of advantages over methods based on the variation of reflection coefficient, even in the case of single-layer disk.

It is another object of the invention to reduce the precision requirements to pit
10 production as compared to existing CD-ROM's. For example, changing the pit size by 100 nm does not hinder reading from the fluorescence disk, while resulting in the complete disappearance of the reflection disk signal.

It is a further object of the invention to provide fluorescence disk insensitivity to disk plane tilt variations up to 1° , which is absolutely inadmissible for the reflection disk.

15 It is a still further object of the invention to provide a 3D optical memory carrier in the form of a multilayer disk.

To achieve these and other objects, the construction principle of a multilayer optical disk with fluorescence-based reading is as follows B. Glushko, US Provisional Patent Application No. 25457, 8/05/97 herein incorporated by reference. Single-layer optical disks
20 with pit-filling fluorescent material as information carrier are sequentially superimposed on one another so that a multilayer system is formed, where active layers consisting of fluorescing pits 0.5 to 1 μm deep alternating with inactive separation layers 20 to 50 μm thick, the latter being transparent for both the excitation laser light and the fluorescence light.

Still another object of the present invention is to develop a fluorescent composition exhibiting physical and physicochemical properties needed for use in CD-ROM type optical disks, including those intended for a 3D optical memory with fluorescence reading, where data carriers represent pits filled with fluorescent composition.

5 This fluorescent composition consisting of fluorescent dye, film-forming polymer, organic solvent, plastifier and (if necessary) surfactant and light stabilizer provides forming active layers of CD-ROM's with fluorescence reading, free from the drawbacks of prior art optical disks with active layers based on polymer films containing organic dyes.

This object is achieved by devising a composition including:

- 10 – A fluorescent dye whose absorption band coincides with the wavelength of the laser emission used for reading, this dye having a high quantum yield of fluorescence, forming a true solution with a polymer matrix and not migrating from the matrix;
- 15 – A film-forming polymer which exhibits a high transparency and does not scatter the laser emission and fluorescent light passing through the active layer, penetrates the substrate pits well and can easily be removed from the substrate;
- 20 – An organic solvent that provides good solubility of the fluorescent composition components, wets the pit-containing substrate surface, does not interact with substrate material and does not produce deformation of pits;
- A plastisizer which increases the elasticity of composition and helping its penetration into the pits.

Also, if necessary, the composition may be completed with surfactants that reduce the surface tension of the composition and thus improve substrate surface wetting and penetration of the solution into the pits; and with light-stabilizers, contributing to the preservation of

The fluorescent composition used for the manufacture of CD-ROM type optical disks, including those intended for the 3D optical memory with fluorescence reading, where pits filled with this fluorescent composition play the role of data carriers, is produced as follows:

First, solutions of fluorescent dye, film-forming polymer, plasticizer, surfactant and
5 light-stabilizer in appropriate solvents are prepared.

Then these solutions are mixed together, homogenized and filtered. After deaeration, a transparent solution is obtained with the following concentration values: film-forming polymer 0.2 – 5.0 wt. %, fluorescent dye 0.001 – 0.1 mole/kg, plasticizer 1.0 – 50 wt. % w.r.t. the polymer, surfactant 0.01 – 2.0 wt. % w.r.t. the polymer, and light-stabilizer 0.1 – 2.0 wt.
10 % w.r.t. the polymer. The fluorescent composition solution is applied by spin coating, roller coating, or dip coating to the surface of substrate representing a pitted disk made from polycarbonate or PMMA.

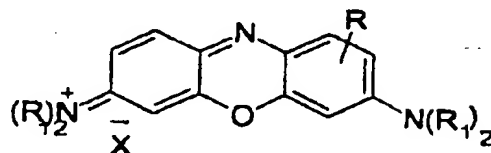
The coating is applied so that the pits are filled with the composition, while the substrate surface among the pits remains uncolored and does not fluoresce. When necessary,
15 the remaining fluorescent composition is removed from the substrate surface by rinsing with a solvent or mechanically.

To produce a multilayer disk intended for the 3D optical memory with fluorescence reading, single-layer disks whose pits are filled with fluorescent composition are sequentially glued to one another in such a way that the active layers consisting of fluorescent pits 0.1 –
20 1.0 μm deep (preferably, 0.3 – 0.5 μm deep) alternate with inactive separation layers 20 to 50 μm thick, these layers being transparent for the laser excitation and fluorescent light wavelengths.

The following compounds are used for fluorescent dyes:

where R stands for H, CH₃, C₂H₅; R₁ stands for H, C₆H₅; R₂ stands for H, Alkyl; R₃ stands for H, CH₃; and X is an anion selected from F, Cl, Br, I, HCOO, CH₃CHOHCOO, ClO₄, etc..

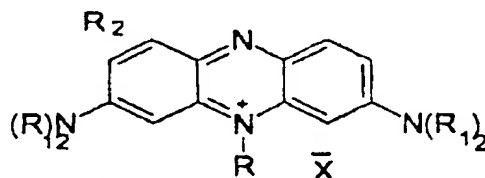
4. Oxazine dyes of the general structure IV



IV

where R stands for H, CH₃, and benzo-group; R₁ stands for H, CH₃, C₂H₅; and X is an anion selected from Cl, Br, I, HCO₂, CH₃CHOHCO₂, ClO₄, etc..

5. Azine dyes of the general structure V



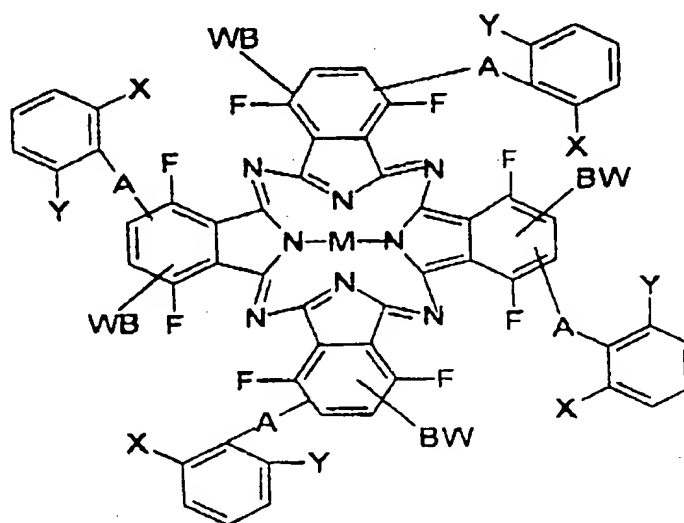
V

where R stands for phenyl, naphthyl; R₁ stands for H, alkyl, phenyl; R₂ stands for H, benzo-group; R₃ stands for H, SO₃H; and X is an anion.

6. Indigoide dyes of the general structure VI

where $Y_1 = Y_2$, $Y_1 = Y_2$, Y_1 and Y_2 stand for O, S, N-Alk, N-Ar, $C(CH_3)_3$; R and R_1 stand for Alk, Ar; $R_2 - R_3$ are various substituents, including those forming cyclic groups; X is an anion; $n = 1 - 3$

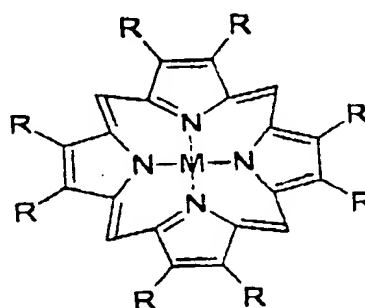
9. Phthalocyanine dyes containing the structure X



X

where A, B stand for O, S; W stands for Alk; X stands for COOR; Y stands for Alk, AlkO, COOR; M stands for 2H, metal, metal oxide, metal halide.

10. Porphyrins of the structure XI



XI

where R stands for H, CH₃; R₁ and R₂ stand for Alk; R₁ stands for Alk; R₂ stands for H; and n/m = 1 to 4. This group includes polymethylmetacrylate, polybutylmetacrylate, and methylmetacrylate- or butylmetacrylate-metacrylic acid copolymers.

3. Cellulose ethers and esters of the general structure [C₆H₇O₂(OR)₃]_n (XIV) and
5 [C₆H₇O₂(OCOR)₃]_n (XV), respectively, including ethyl cellulose with $\gamma = 230 - 260$ (where γ is the number of substituted hydroxyl groups per 100 glycoside residues of the cellulose macromolecule), cellulose acetobutyrate, and cellulose nitrate (with a nitrogen content of 9 – 11 %).

Apart from this, phenol-formaldehyde resins (resols and novolacs), melamine-
10 formaldehyde resins, urea-formaldehyde resins, and polyvinylacetate may be used as film-forming polymers for fluorescent compositions.

Solvents being used for fluorescent compositions wet the substrate surface well, help composition penetration into the pits, but do not interact with the substrate material and produce no pit deformation. When polycarbonate disks are used, only dioxane and aliphatic
15 alcohols, methanol, ethanol, propanol, isopropanol, isobutanol, pentanol and their mixtures may be used as solvents.

Film-forming polymers proposed in the present invention exhibit various ranges of a highly elastic state and, therefore, provide different plasticity of coatings. An inadequate plasticity of the polymer hinders the penetration of the fluorescent composition in small pits
20 of size 0.1 – 1.0 μm . In such cases, plastifiers are used. As plastifiers allow the decrease of the flow point and glass transition temperature, as well as the elasticity modulus of fluorescent composition, proposed are phthalic esters (including dibutyl phthalate and dioctyl phthalate), sebacic esters (including dibutyl sebacate and di-(2-ethyl-hexyl) sebacate), and

Triton X-45	1.0
Tinuvin 292	10

These alcohol solutions are mixed in proportions providing the following concentrations of components:

Compound	Concentration
Polyvinylbutiral (PVB)	10 g/l
Oxazine 1	1.3 wt. % w.r.t. PVB
Diocetyl phthalate	20 wt. % w.r.t. PVB
Triton X-45	0.03 wt. % w.r.t. PVB
Tinuvin 292	0.5 wt. % w.r.t. PVB

The composition solution is filtered, allowed to stand at 40°C for aeration and applied by spinning to a pitted polycarbonate disk at 60°C. Having been exposed for 20 minutes, the
5 fluorescent composition layer is treated with ethyl alcohol for 20 seconds while remaining on the spinner. The produced fluorescence disk has the data pit background noise contrast ratio $\gamma = 6$, as compared to $\gamma = 1.3$ for usual disks with reflection-based reading. The fluorescent composition has an absorption maximum at 645 nm and a fluorescence maximum at 680 nm and is therefore suitable for fluorescence reading by diode laser with an emission wavelength
10 of 640 nm.

Example 2

A composition similar to that of Example 1, except that Nile blue (perchlorate) is used as a fluorescing dye. A 6.3-g/l solution in ethyl alcohol is taken in proportion giving a concentration of 1.0 wt. % w.r.t. PVB. The produced fluorescence disk has a contrast ratio $\gamma =$

Example 6

Compositions similar to those in Example 5, except that 5-g/l solution of polyvinylacetate is used as a film-forming polymer. Using oxazine 1 as a fluorescent dye gives $\gamma = 9$, Nile blue gives $\gamma = 8$, HIDC (iodide) gives $\gamma = 10$, and HITC (perchlorate) gives $\gamma = 9$.

Example 7

To produce a multilayer optical disk of CD ROM type with fluorescence reading, as shown in Fig. 1, a single-layer disk 1 of 120 μm thickness with pits 3 filled with the fluorescent composition 5 prepared according to Example 1, 2, 3, 4, 5 or 6 is covered with a layer 7 of UV-69 adhesive, and a similar fluorescence disk 9 with a polycarbonate substrate of 30 μm thickness is glued thereto. The adhesive is cured with UV light 11. In just the same way, as shown in Fig. 2, another eight disks 9 similar to the second one are sequentially glued. This process gives a 10-layer fluorescence disk 13 with the bottom layer contrast ratio at least .5.

While various embodiments have been set forth above, those skilled in the art who have reviewed this disclosure will readily appreciate that other embodiments can be realized within the scope of the present invention. For example, disclosures of the number and thicknesses of layers, the concentrations of various materials, the choice of a substrate material, and the like should be understood as illustrative rather than limiting. Therefore, the present invention should be construed as limited only by the appended claims.

7. The fluorescent composition of claim 1, wherein the plasticizer is in a concentration of 1.0 – 50.0 wt. % with respect to film-forming polymer.

8. The fluorescent composition of claim 7, wherein the plasticizer is selected from the group consisting of phthalic esters, sebacic esters, and phosphate esters.

5 9. The fluorescent composition of claim 1, wherein the surfactant comprises a non-ionogenic compound in a concentration of 0.01 – 2.0 wt. % with respect to film-forming polymer.

10 10. The fluorescent composition of claim 2, wherein the light stabilizer comprises HALS (Hindered Amine Light Stabilizer) in a concentration of 0.1 – 2.0 wt. % with respect to the film-forming polymer.

11. The fluorescent composition of claim 1, wherein the organic solvent is selected from the group consisting of methanol, ethanol, isopropanol, pentanol and mixtures thereof.

12. A method of manufacturing a CD-ROM type optical disk, the method comprising:
providing a substrate which is formed as a disk which has a surface and is covered with
15 pits in the surface; and

applying a fluorescent composition by spin coating, roller coating, or dip coating to the surface of the substrate so as to fill the pits with the fluorescent composition, while the surface outside the pits remains free of the fluorescent composition and does not fluoresce.

13. The method of claim 12, wherein the pits are 0.1-1.0 micrometers deep.

20 14. The method of claim 13, wherein the pits are 0.3-0.5 micrometers deep.

15. A method of manufacturing a multilayer CD-ROM type optical disk the method comprising:

22. A fluorescent CD-ROM optical disk comprising at least one substrate, said substrate containing pits wherein said pits are filled or coated with a fluorescent composition, said fluorescent composition comprising a fluorescent dye, a film-forming polymer and a plasticizer.
23. The optical disk of claim 22 wherein the fluorescent composition further comprises a surfactant and a light stabilizer.
24. The optical disk of claim 23, wherein the fluorescent dye of the fluorescent composition is in a concentration of about 0.001 - 0.1 mole per kg of the film forming polymer.
25. The optical disk of claim 22 wherein the film forming polymer is in a concentration of about 2.0 - 50.0 g/l.
26. The CD-ROM optical disk of claim 25 wherein the film forming polymer is selected from the group consisting of polyvinylacetals, acrylic resins, cellulose ethers, cellulose esters, phenol-formaldehyde resins, melamine-formaldehyde resins, urea-formaldehyde resins, and polyvinylacetate.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US98/23625

A. CLASSIFICATION OF SUBJECT MATTER:

US CL :

252/301.35, 301.34; 427/157; 396/288, 283, 275.4, 101; 420/270.14, 270.15, 270.18, 270.19, 270.2, 270.21